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# मानक

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Mazdoor Kisan Shakti Sangathan

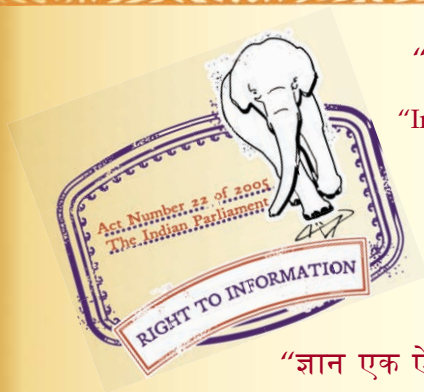
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“Step Out From the Old to the New”

IS 1350-5 (1979): Methods of Test for Coal and Coke, Part V: Special Impurities [PCD 7: Solid Mineral Fuels]



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Bhartrhari—Nitiśatakam

“Knowledge is such a treasure which cannot be stolen”



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IS : 1350 ( Part V ) - 1979  
( Superseding IS : 1352 - 1959 )  
( Reaffirmed 1986 )

*Indian Standard*  
METHODS OF TEST  
FOR COAL AND COKE  
PART V SPECIAL IMPURITIES  
( *First Revision* )

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BUREAU OF INDIAN STANDARDS  
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG  
NEW DELHI 110002

*Indian Standard*  
**METHODS OF TEST  
FOR COAL AND COKE**  
**PART V SPECIAL IMPURITIES**  
*( First Revision )*

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( Continued on page 2 )

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## IS: 1350 ( Part V ) - 1979

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*Indian Standard*  
**METHODS OF TEST  
FOR COAL AND COKE**  
**PART V SPECIAL IMPURITIES**  
*( First Revision )*

**0. FOREWORD**

**0.1** This Indian Standard was adopted by the Indian Standards Institution on 15 May 1979, after the draft finalized by the Solid Mineral Fuels Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

**0.2** This standard was first published as IS : 1352-1959 'Methods of test for coal and coke — special impurities'. However, in this revision method of determination of sulphur given in 5 of the original standard has been deleted as this has been included in IS : 1350 ( Part III )-1969\* and the method for determination of arsenic in coal has now been based on the use of silver diethyldithiocarbamate reagent which makes a quantitative determination possible. Since this standard is now being revised and issued as Part V of IS : 1350, IS : 1352-1959 stands withdrawn.

**0.3** In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960†.

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**1. SCOPE**

**1.1** This standard ( Part V ) prescribes the methods for determination of special impurities in coal and coke, namely, carbon present, as carbonate, chlorine, phosphorus and arsenic.

**2. QUALITY OF REAGENTS**

**2.1** Unless specified otherwise, pure chemicals and distilled water ( *see* IS : 1070-1977‡ ) shall be employed in analysis.

**NOTE** — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the results of test.

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\*Methods of test for coal and coke: Part III Determination of sulphur ( *first revision* ).

†Rules for rounding off numerical values ( *revised* ).

‡Specification for water for general laboratory use ( *second revision* ).

## IS : 1350 ( Part V ) - 1979

**2.1.1** For the determination of arsenic ( *see* 7 ) all the reagents shall be free from arsenic.

### 3. SAMPLING

**3.1 Methods of Sampling** — Methods of sampling shall be as prescribed in IS : 436 ( Part I/Sec 1 )-1964\* for coal and IS : 436 ( Part II )-1965† for coke.

#### 3.2 Preparation of Samples for Test

**3.2.0 General** — Methods of sampling prescribed in IS : 436 ( Part I/Sec 1 )-1964\* and IS : 436 ( Part II )-1965† shall be followed in the preparation of samples sent to the laboratory. Besides the laboratory samples to be used for the analysis of coal and coke, special samples are recommended for moisture.

**3.2.1** The samples prepared in accordance with IS : 436 ( Part I/Sec 1 )-1964\* and IS : 436 ( Part II )-1965† shall be received in sealed containers and shall consist of the following:

- a) Analysis sample of about 300 g of air-dried coal or coke, ground to pass 212-micron IS Sieve; and
- b) Special moisture sample of 1 kg of same coal or 2.5 kg of coke, crushed to pass the square mesh screen conforming to designation 12.5 mm (C) of IS : 460-1962‡ to be sent in duplicate.

**3.2.2** Where air-drying has been adopted in the preparation of the samples the percentage loss of moisture in this operation shall be recorded on the label together with the method of sampling used.

**3.2.3** Samples received in the laboratory if already, ground to pass 212-micron IS Sieve shall be re-sieved to verify that all the material passes through this sieve, and then air-dried for 24 hours and mixed and bottled as above. Should a sample of coal or coke be transported to any distance between the point of preparation and the laboratory under conditions in which it may be shaken down and may cause segregation to any degree, the entire contents of the bottle shall be re-mixed before analytical work is started. The use of mechanical devices is recommended.

**3.2.4** Certain coals may be found to give irregular results on analysis. In such cases, and for analytical work only, the analysis sample should be further ground to pass 125-micron IS Sieve and re-mixed. This final grinding is normally found to ensure reasonable agreement between repeat

\*Methods for sampling of coal and coke: Part I Sampling of coal, Section 1 Manual sampling ( *revised* ).

†Methods for sampling of coal and coke: Part II Sampling of coke ( *revised* ).

‡Specification for test sieves ( *revised* ).

determinations. The normal method of mixing coal in the laboratory is to roll it on a sheet of rubber cloth and turn it over at intervals with a large spatula or flat spoon. This method is not entirely satisfactory, since the movement of the coal tends to cause segregation. The difficulty may be overcome in part by spreading the mixed sample in a thin layer and filling the analysis bottle by means of small increments taken with the spoon from places spaced uniformly over the surface of the layer. This method of filling is particularly necessary when more than one bottle is being filled. A laboratory mechanical mixer is, however, preferable.

#### 4. CARBON PRESENT IN COAL AS CARBONATE

**4.0 General** — Certain coals contain appreciable quantities of metallic carbonates, the carbon dioxide component of which may represent as much as one percent of the coal. When such coals are analysed, this carbon dioxide component should be determined and the carbon equivalent deducted from the determined percentage of carbon as shown under 5.1 of IS : 1350 ( Part IV/Sec 1 )-1974\*. The pressure method ( *see* 4.1 ) gives an accurate result in 15 to 20 minutes while the volume ( *see* 4.2 ) takes longer time.

#### 4.1 Pressure Method

**4.1.1 Apparatus** — The apparatus is shown in Fig. 1. It comprises:

- a) *Reaction vessel* — of 50 to 100 ml capacity, either a carbon dioxide flask *A*, fitted with ground glass joint and a short piece of capillary tubing *B*, or a specific gravity bottle with a 12.5 mm wide ground glass neck with a stopper having a capillary.
- b) *Acid container, C* — a flat-bottomed glass tube, of 15 ml capacity and capable of passing through the neck of the reaction vessel.
- c) *Silica gel guard tubes ( D and E )* — with a length of pressure tubing to connect to the reaction vessel and to the stopcock.
- d) *Capillary U-gauge, F* — 1 to 2 mm bore, to read up to 40 cm of mercury. On the upper part of one limb of the U-gauge, the bore may be widened to allow space for the mercury to accumulate while being sucked from the other end. The effective volume also will remain unaltered ( *see* Fig. 1 ).
- e) *Two-way stopcock*
- f) *Suction flask, G*
- g) *Water pump*

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\*Methods of test for coal and coke: Part IV Ultimate analysis, Section 1 Determination of carbon and hydrogen ( *first revision* ).

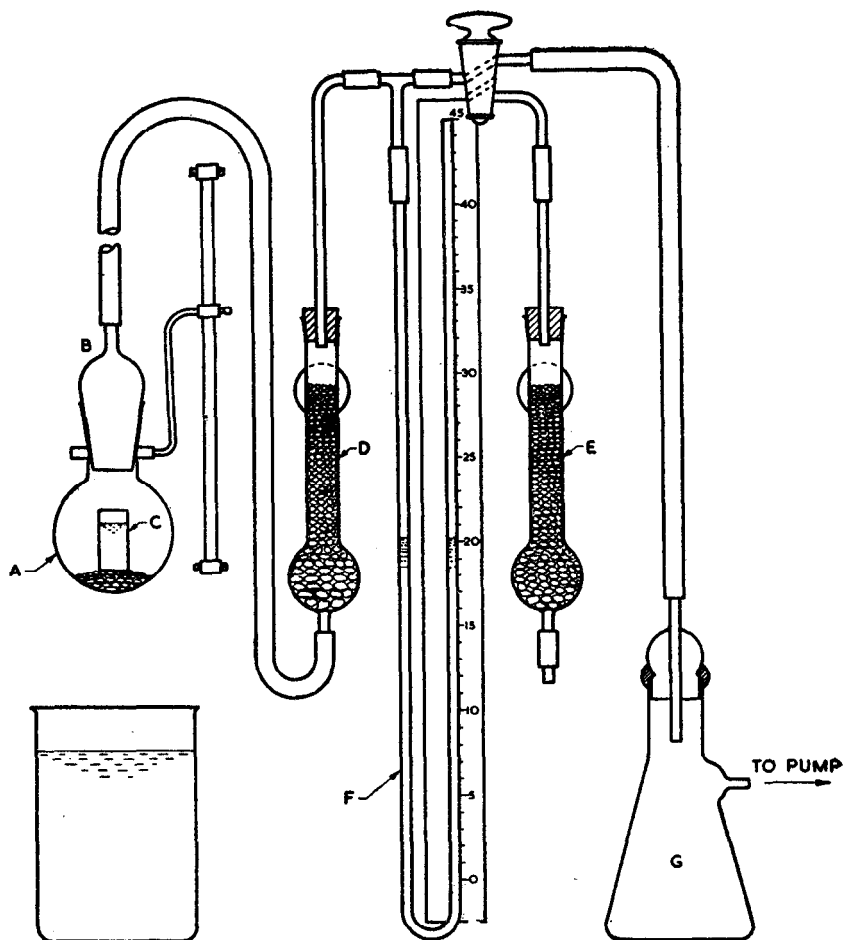


FIG. 1 ASSEMBLY OF THE APPARATUS FOR THE DETERMINATION OF CARBON DIOXIDE ( PRESSURE METHOD )

#### 4.1.2 Reagent

**4.1.2.1 Dilute hydrochloric acid** — approximately 5 N ( or one part of concentrated hydrochloric acid and one part of distilled water ) containing 0.5 percent of a wetting agent\*.

**4.1.3 Standardization and Calibration** — Weigh 0.120 g of anhydrous sodium carbonate, which has been previously dried for one hour and stored in a

\*Permalin is a suitable wetting agent.

desiccator over anhydrous magnesium perchlorate or concentrated sulphuric acid. Add 14 ml of dilute hydrochloric acid to the acid container and place this in the reaction flask. Carry out the test as described under 4.1.5.

NOTE — 4 ml of extra acid that is equal to the volume of 5 g of coal is added. This is the volume which is normally used in a test (see 4.1.5).

**4.1.4 Calibration** — The pressure, obtained in the standardization test is equivalent to the pressure from 5 g of coal, of one percent carbon dioxide. The point represented by this pressure on a graph joined to the origin gives a calibration curve, from which values of observed results can be read. The calibration may be checked by repeating the determination with different mass of anhydrous sodium carbonate not exceeding 0.120 g.

**4.1.5 Procedure** — Thoroughly mix for one minute the air-dried material ground to pass through 212-micron IS Sieve preferably with a laboratory mechanical mixer. Weigh accurately 5 g of the material on a tared scoop and pour into the reaction flask *A*. Measure 10 ml of dilute hydrochloric acid into the acid container *C*, and rest it on the coal in the flask. Connect the reaction flask to the gauge *F*, through the guard tube *D*, evacuate to 40 cm mercury, immerse for 7 minutes in a beaker of water held at the same temperature as was used in the standardization test (see 4.1.3). During the last 4 minutes the pressure should not alter by more than 0.1 cm (gas-tightness test). Spill the acid on the coal and heat the reaction vessel gently for 3 minutes over a naked gas flame about 12 mm in height, using a small Bunsen burner with the tube removed, care being taken to avoid pressure in the apparatus. Immerse the flask for 7 minutes in a beaker of water at the same temperature as was used in the standardization test and read the pressure. Read off the percentage of carbon dioxide from the calibration curve.

**4.1.6 Precaution for Material Containing Decomposable Monosulphides** — If the material contains a monosulphide which reacts with hydrochloric acid to evolve hydrogen sulphide, the latter can be absorbed by the addition of 5 ml of concentrated mercuric chloride solution, allowance being made for the change in volume of the gas space due to the presence of the extra volume of liquid.

**4.1.7** With coals of high carbonate contents, a positive pressure develops inside the apparatus. This should be overcome by reducing the quantity of coal, a corresponding amount of distilled water being added to compensate for the reduced volume.

## 4.2 Volume Method

**4.2.1 Apparatus** — An assembly of the apparatus is shown in Fig. 2. It consists of the following:

- a) *Haldane gas analysis apparatus* — 21 ml capacity.

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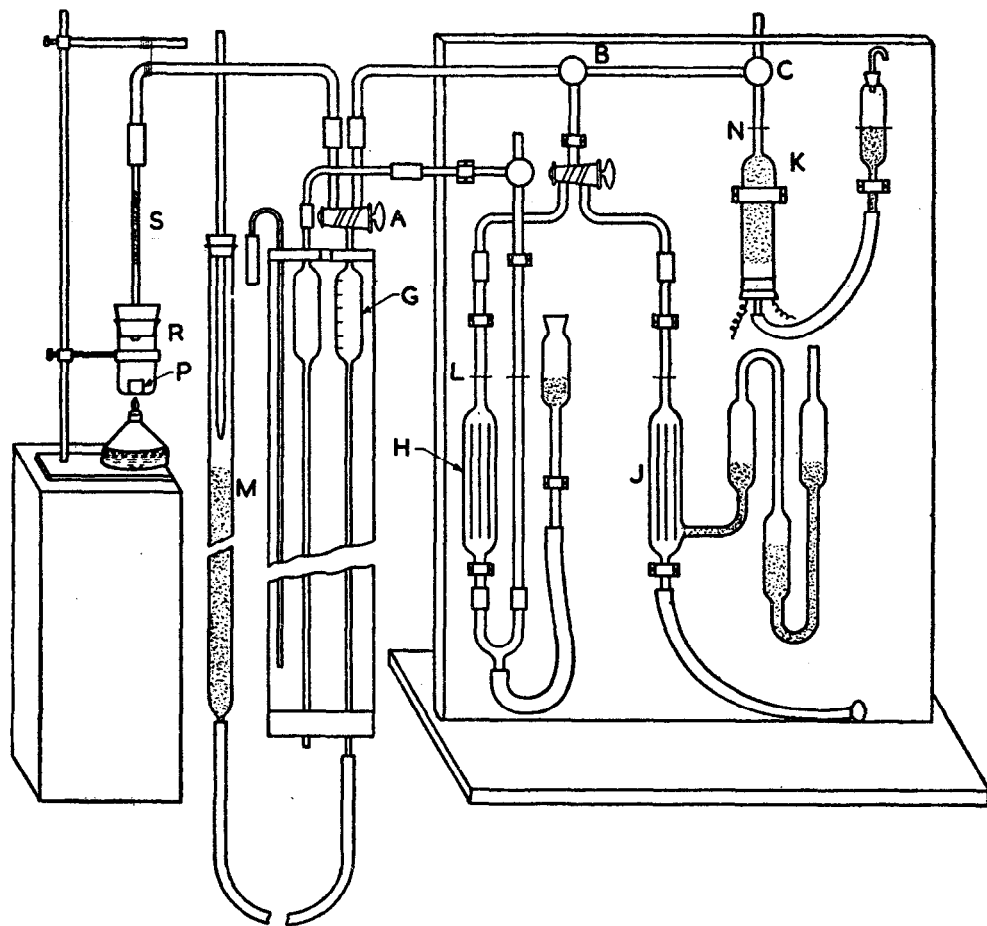


FIG. 2 ASSEMBLY OF APPARATUS FOR THE DETERMINATION OF CARBON DIOXIDE  
(CFRI METHOD)

- b) *Reaction vessel*—weighing bottle or beaker *R*, 20 to 25 ml capacity, fitted with a one-holed rubber cork.
- c) *Glass tubing*, *S* — 6 mm external diameter.
- d) *Pressure tubing* — connecting *S* to the burette *G*, and suspended by a stout wire.
- e) *Glass container*, *P* — of about 3 ml capacity.

NOTE — The tap *A* on the Haldane apparatus should be a good fit lubricated with a little apiezon grease to withstand the vacuum applied.

#### 4.2.2 Reagents

- a) *Dilute hydrochloric acid* — approximately 3 N.
- b) *Wetting agent solution* — a 0.5 percent solution of a suitable wetting agent\*.
- c) *Potassium hydroxide solution* — 10 percent (*m/v*).

#### 4.2.3 Procedure

- a) Accurately weigh into the reaction vessel *R*, a quantity of the material ( *see* Note ) ground to pass 212-micron IS Sieve sufficient to give rise to about 3 ml of carbon dioxide.

NOTE — For coals having one percent carbon dioxide content, 0.5 g will give rise to some 3 ml of carbon dioxide.

- b) Pour two millilitres of the dilute hydrochloric acid in the container *P*, add two drops of the wetting agent solution and place the container and acid in the reaction vessel *R*, taking care that the acid does not spill. Cork *R* firmly, and connect to the graduated burette *G*, as shown. Keep the mercury in the burette moist as usual with a drop of distilled water. Evacuate the system *R* and *G*, by alternately lowering *M* ( to 20 ml mark ) and discharging evacuated air to atmosphere at *C*. Repeat four or five times to obtain a vacuum of about 70 cm of mercury. Next admit air through *C* to *G* until the reading on *G* is between 15 and 16-ml marks at atmospheric pressure. Close *C*, and open *G* to the potash gauge *H*; pass the air through potash to absorb the carbon dioxide present in it and then return the air to *G*. Now connect *G* to *R*, and tilt *R* so that the acid flows on to the material. After one or two minutes, warm *R* by a small flame ( a spirit lamp may be used ) and shake it gently but thoroughly. Regulate the heat to keep the liquid just boiling for some 5 minutes. Next remove the flame and allow the vessel to cool a little, but while the liquid is still warm, draw the gases 3 or 4 times from *R* into *G*, transferring each withdrawal from *G* into the combustion pipette *K*.

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\*Permal, Teepol and Lissapol are suitable wetting agents.

- c) Finally bring the gases back from *K* into *G*. Stir the water in the burette jacket by bubbling air through it for two minutes to give constant temperature, equalize the mercury levels in *M* and *G*, and open carefully to the potash gauge as before. Note the volume of gas. Next absorb the carbon dioxide in the potash. Then open *G* to *R* and again warm *R* and draw off the gases under reduced pressure and pass them, as previously, into *K*. Repeat the operation 3 or 4 times to get increased vacuum ( 70 cm Hg ). Absorb the carbon dioxide as before. If there is appreciable carbon dioxide absorption at this stage, return the gases once again to the vessel *R*, boil the liquid for another 2 to 3 minutes under reduced pressure, and absorb as before any carbon dioxide which might have evolved. Repeat the operations, if the quantity of carbon dioxide in the last absorption is not below 0.01 ml in order to ensure that all the carbon dioxide has been evolved. Note the volume of gas after equalizing the levels in *M* and *G*. Note the temperature of the jacket water, and the barometric pressure.

#### 4.2.4 Precaution — See 4.1.6.

#### 4.2.5 Calculation

- a) Volume of carbon dioxide ( at NTP )

$$V = D \frac{273 (B - e)}{(273 + t) 760}$$

where

*D* = drop in volume in ml due to carbon dioxide absorption;

*B* = barometric pressure;

*e* = aqueous tension at *t*°C; and

*t* = temperature in degree Celsius

- b) Carbon dioxide, percent by mass =  $V \frac{196.5}{1\,000\,M}$

where

*V* = volume in ml of carbon dioxide ( NTP ), and

*M* = mass in g of the material taken for the test.

**4.2.6 Occluded Gases in Coal** — Methane may be liberated from freshly mined coal when evacuated and warmed. Using the absorption method, however, the evolution of such gas does not cause error. Moreover, the gases drawn off can later be determined, in the combustion pipette if it is desired to see whether combustible gas is present or not.

## 5. PHOSPHORUS IN COAL AND COKE

**5.0 General** — There are two methods, one gravimetric ( phosphomolybdate ) and the other volumetric. A sample of the coal or coke is completely converted into ash and a known mass of the ash is heated with a mixture of hydrofluoric and nitric acids to remove silica which escapes as silicon tetrafluoride while phosphorus is retained in solution as phosphoric acid.

### 5.1 Determination of Phosphorus by the Gravimetric ( Phosphomolybdate ) Method

**5.1.0 Outline of the Method** — The phosphoric acid in the aqueous extract is precipitated as ammonium phosphomolybdate which is then weighed to determine the percentage by mass of phosphorus. From the value of ash determined as prescribed under 8 of IS: 1350 ( Part I )-1969\* and the results now obtained, the percentage of phosphorus in the air-dried prepared sample is calculated.

#### 5.1.1 Apparatus

**5.1.1.1 Crucible** — two; one of platinum of 30-ml capacity with lid; and the other of sintered glass ( G No. 3 ).

#### 5.1.2 Reagents

**5.1.2.1 Concentrated nitric acid** — relative density 1.42 ( see IS: 264-1976† )

**5.1.2.2 Dilute nitric acid ( I )** — relative density 1.20, prepared by diluting 390 ml of concentrated nitric acid with water to one litre.

**5.1.2.3 Dilute nitric acid ( II )** — obtained by diluting 1.5 volumes of concentrated nitric acid with water to 100 volumes.

**5.1.2.4 Hydrofluoric acid** — a solution in water containing about 550 g of hydrogen fluoride per litre and free from phosphorus.

**5.1.2.5 Phenolphthalein indicator** — prepared by dissolving 0.1 g phenolphthalein in 80 ml of ethyl alcohol and diluting with water to 100 ml, then filtering.

**5.1.2.6 Sodium hydroxide solution** — approximately 0.1 N.

**5.1.2.7 Concentrated ammonium hydroxide** — relative density 0.90.

**5.1.2.8 Potassium nitrate** — solid.

\*Methods of test for coal and coke: Part I Proximate analysis ( *first revision* ).

†Specification for nitric acid ( *second revision* ).

**5.1.2.9 Ammonium molybdate solution** — Dissolve 100 g of pure molybdic acid (containing not less than 85 percent of  $\text{MoO}_3$ ) in a mixture of 400 ml of cold water and 80 ml of concentrated ammonium hydroxide solution. Mix the solution by shaking and pour slowly into a solution of 400 ml of concentrated nitric acid in 600 ml of water, contained in a flask. Mix by shaking during the addition. Add to the mixture about 0.05 g of micro-cosmic salt  $[\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}]$ , dissolved in a small quantity of water. Heat the mixture gently to  $65^\circ\text{C}$  shaking frequently. Allow the solution to cool, and leave it to stand overnight, then decant the clear supernatant liquid into a dark brown stoppered bottle. Do not keep the reagent longer than two months.

**5.1.2.10 Dilute ammonium nitrate solution** — containing 3 g of ammonium nitrate and 1.5 ml of nitric acid (relative density 1.20) dissolved in 100 ml of water.

**5.1.2.11 Absolute alcohol** — See IS : 321-1964\*.

**5.1.3 Procedure** — In the following method it is assumed that all the phosphorus has been retained in the ash. The various stages of the procedure are described below.

**5.1.3.1 Extraction with a mixture of nitric acid and hydrofluoric acid** — Grind the ash in an agate mortar to pass through IS Sieve 63-micron. Carry out a preliminary determination using 0.5 g of ash and depending upon the phosphorus content, weigh the appropriate quantity of the ash into a platinum crucible, as follows:

Phosphorus Content of Ash, percent	Mass in g of Ash to be Taken
Less than 0.1	1.0
0.1 to 0.25	0.5
0.25 to 0.5	0.4
0.5 to 0.75	0.25
0.75 to 1.0	0.2
Greater than 1.0	0.1

**5.1.3.2** Add carefully 10 ml of concentrated nitric acid and 5 ml of hydrofluoric acid and cautiously evaporate to dryness during a period of about 45 minutes, preferably on a hot plate or a hot sand bath. The sand for this purpose is to be extracted previously with acid. Add a further 10 ml of concentrated nitric acid and 5 ml of hydrofluoric acid, digest and evaporate to dryness as before. To ensure complete removal of the hydrofluoric acid, add further 5 ml of concentrated nitric acid and again evaporate to dryness. Carry out all evaporations, with the crucible partly

\*Specification for absolute alcohol (revised).

covered with the lid in order to avoid error due to accidental 'spitting'. Do not ignite at any stage. Add 15 ml of dilute nitric acid (I) to the crucible and evaporate the contents to about 7 ml. Transfer the solution to a 250-ml beaker and wash the crucible with water, adding the washings to the contents of the beaker. The combined volume of the washings and the original solution should be about 80 ml. Cover the beaker with a clock glass and boil the contents of the beaker for 15 minutes, allowing a glass rod to stand in it to inhibit bumping.

**5.1.3.3 Filtration of extract** — Filter the extract obtained as above through a thick, general purpose, fine filtering, 9 cm diameter filter paper (Whatman No. 3) into a 400-ml beaker and wash the filter paper with water, collecting the washings until they are free from acid, that is, until 10 ml of the final washings give an alkaline reaction with one drop of phenolphthalein and one drop of sodium hydroxide solution. The final volume of the filtrate should be about 250 ml.

**5.1.3.4 Precipitation** — Evaporate the solution to about 50 ml. Add concentrated ammonium hydroxide solution carefully drop by drop with continual rotation of the contents of the beaker until a slight permanent precipitate of iron and aluminium hydroxide appears. Redissolve this precipitate by addition of the minimum quantity of concentrated nitric acid keeping the contents of the beaker agitated, and finally add 4 ml excess of concentrated nitric acid and 3 to 4 g of potassium nitrate. The volume of the liquid should not now exceed 70 ml. Heat the contents of the beaker to 75°C, and slowly add 30 ml of ammonium molybdate solution, previously heated to 55°C, in a thin, stream, with constant agitation of the liquid. Maintain at 50°C for 30 minutes. Keep the beaker containing the phosphomolybdate precipitate, with occasional stirring for 2.5 hours at room temperature (25 to 30°C), allow it to settle and then filter the precipitate through the weighed sintered-glass crucible. Wash the phosphomolybdate precipitate 4 times with weak nitric acid (II) using 15 ml each time, twice with dilute ammonium nitrate solution using 15 ml each time, twice with water using 5 ml each time and finally, 3 times with absolute alcohol using 3 ml each time. Dry at 125 to 130°C in an oven for 30 minutes and cool in a freshly charged desiccator containing concentrated sulphuric acid. Repeat till the mass is constant.

**5.1.3.5** Carry out a blank determination exactly as described above but substituting a pure phosphorus compound diluted to contain an amount of phosphorus approximately equal to that in the ash.

**5.1.4 Calculation** — One gram of ammonium phosphomolybdate contains 0.0165 g of phosphorus:

$$\text{a) Phosphorus, percent by mass, in the ash (A)} = \frac{1.65 [X - (V - 60.6 Z)]}{M}$$

where

$X$  = mass in g of the phosphomolybdate precipitate, .

$V$  = mass in g of the phosphomolybdate precipitate obtained from the pure phosphorus compound,

$Z$  = calculated mass in g of the phosphorus taken for the blank determination, and

$M$  = mass in g of the ash taken for the test.

b) Phosphorus, percent by mass in the coal ( $P$ ) =  $0.01 A \times C$

where

$A$  = percent by mass of phosphorus in ash [ see 5.1.4(a) ], and

$C$  = percent by mass of ash in the coal.

## 5.2 Determination of Phosphorus by the Volumetric Method

**5.2.0 Outline of the Method** — Phosphorus is precipitated as phosphomolybdate, filtered and dissolved in standard alkali. The excess alkali is estimated by titration with a standard acid and from the titre value the percentage by mass of phosphorus in the ash is calculated.

**5.2.0.1 Error due to the presence of arsenic in the amounts normally present in coal are insignificant.** The inhibiting effect of titanium is reduced to negligible proportions by the strengths of the nitric acid and the ammonium molybdate used. In cases where interference due to arsenic is believed to be significant, the following precautions may be taken:

a) Digest the coal ash with a mixture containing ferric chloride, hydrochloric acid and hydrogen bromide to expel the arsenic as the volatile arsenious chloride.

b) Carry out the phosphomolybdate precipitation at 50°C.

### 5.2.1 Apparatus

**5.2.1.1 Crucible** — of platinum of 30 ml capacity with lid.

**5.2.1.2 Conical flask** — of 500 ml capacity fitted with rubber bung, glass tubes and thermometer (0 to 100°C) ( see schedule Mark 4 of IS : 2480-1973\* ).

**5.2.1.3 Soda lime guard tube**

### 5.2.2 Reagents

**5.2.2.1 Concentrated nitric acid** — relative density 1.42.

**5.2.2.2 Nitric acid** — See 5.1.2.2.

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\*Specification for solid stem general purpose glass thermometers (first revision).

**5.2.2.3 Standard nitric acid** — approximately 0.1 N standardized as follows:

Place 15 ml of the sodium hydroxide solution into a conical flask and add a hardened retentive filter paper of about 10 cm diameter, that has been previously well washed with the potassium nitrate solution. Dilute to 100 ml with freshly boiled and cooled distilled water and insert the soda lime guard tube. Warm the contents of the flask to 35 to 45°C whilst continuously shaking the flask to disintegrate the filter paper. Cool, remove the guard tube and titrate with the 0.1 N nitric acid, using phenolphthalein as indicator.

**5.2.2.4 Hydrofluoric acid** — See 5.1.2.4.

**5.2.2.5 Potassium nitrate solution** — a neutral aqueous solution containing one gram of potassium nitrate per litre.

**5.2.2.6 Potassium nitrate** — solid.

**5.2.2.7 Phenolphthalein** — See 5.1.2.5.

**5.2.2.8 Standard sodium hydroxide solution** — approximately 0.1 N, standardized using weighed quantities of benzoic acid or oxalic acid.

**5.2.2.9 Concentrated ammonium hydroxide solution** — relative density 0.9.

**5.2.2.10 Ammonium molybdate solution** — See 5.1.2.9.

### 5.2.3 Procedure

**5.2.3.1 Extraction** — Extract the phosphorus in the ash with a mixture of nitric acid and hydrofluoric acid and filter into a 500-ml conical flask (see 5.1.3.1 and 5.1.3.3).

**5.2.3.2** Evaporate the filtered extract till the volume is about 50 ml. Add concentrated ammonium hydroxide solution drop by drop with continual rotation of the contents of the flask, until a slight permanent precipitate of iron and aluminium hydroxide appears. Redissolve this precipitate by addition of the minimum quantity of concentrated nitric acid keeping the contents of the flask agitated and, finally, add 4 ml excess of concentrated nitric acid and 3 to 4 g of potassium nitrate, the volume of the liquid now being not greater than 70 ml. Fit the flask with a clean rubber bung carrying a thermometer and provided with an air vent, the bulb of the thermometer being immersed in the liquid without touching the sides or bottom of the flask.

**5.2.3.3** Heat the contents of the flask to 75°C, remove the bung and add slowly with constant swirling, 30 ml of the ammonium molybdate solution previously heated to 55°C (see 5.1.3.4). Replace the bung carrying the thermometer and continue to swirl the contents of the flask for a further period of two minutes.

**5.2.3.4** Maintain the flask at 50°C for 30 minutes. Allow the flask and contents to cool, and then let them stand for at least three hours but not longer than overnight. Filter off the precipitate on a hardened retentive 10-cm diameter filter paper.

**NOTE** — Instead of a hardened retentive filter paper, a Gooch crucible with a carefully prepared filter pad of acid-free filter paper pulp may be used. Excessive suction should be avoided. In this case, when standardizing the 0.1 N nitric acid ( see 5.2.3.3 ) the hard, slow filtering, filter paper should be replaced by a filter pad ( previously well washed with 0.1 percent potassium nitrate solution ) identical with that used when filtering off the ammonium phosphomolybdate.

**5.2.3.5** Wash with a solution of potassium nitrate until 10 ml of the washings give a strongly alkaline reaction with one drop each of phenolphthalein and 0.1 N sodium hydroxide solution ( about ten washings will be necessary ). It is important to use the minimum amount of washings solution, and to keep the precipitate wetted with it, since the slight solubility of the precipitate is increased by atmospheric oxidation of the phosphomolybdate.

**5.2.3.6** Transfer the filter paper and the precipitate to the original 500-ml conical flask and add 15 ml of the standard sodium hydroxide solution. Dilute the solution to 100 ml by addition of freshly boiled, cooled distilled water and fit the flask with a rubber bung carrying freshly charged soda-lime guard tube to prevent carbonation of the alkali. Warm the contents of the flask to 35 to 40°C and agitate the flask so as to reduce the filter paper to pulp. Cool, remove the bung and the guard from the flask and titrate the excess of sodium hydroxide with standard nitric acid, using phenolphthalein as indicator.

**5.2.3.7** The solution should only be warmed sufficiently to hasten the dissolution of the precipitate. It has been shown that boiling results in loss of ammonia, in which case the conversion factor given for the standard method does not hold. The presence of ammonia, in the solution during titration has no appreciable effect upon the results. The nitric acid should be added carefully, drop by drop, and with constant, swirling of the flask. If, after the solution has turned colourless, a pale-pink colour develops in the solution when the filter paper pulp is allowed to settle, carefully add a further quantity of the acid until the colour just disappears. Record the total titre.

**5.2.3.8** Carry out a blank determination exactly as described above but using a pure phosphorus compound diluted to contain an amount of phosphorus approximately equal to that in the ash.

#### 5.2.4 Calculation

$$\text{a) Phosphorus, percent by mass, in the ash (A)} = \frac{0.0135}{M} (b - a + 740.7 X)$$

where

$b$  = volume in ml of 0.1 N nitric acid used in the blank,

$a$  = volume in ml of 0.1 N nitric acid used in the test,

$X$  = calculated mass in g of phosphorus taken in the blank determination, and

$M$  = mass in g of ash taken.

b) Phosphorus, percent by mass in coal ( $P$ )  $= 0.01 A \times C$

where

$A$  = percentage of phosphorus in ash [ see 5.2.4 (a) ], and

$C$  = percentage of bulk ash in coal.

## 6. CHLORINE IN COAL AND COKE

**6.0 General** — Chlorine is determined by the Eschka method, using the air-dried laboratory sample ground to pass 212-micron IS Sieve.

### 6.1 Eschka Method

**6.1.0 Outline of the Method** — This method for the extraction of chlorine in coal or coke requires the incineration of the sample in the presence of Eschka mixture at 775°C to remove the combustible matter and to convert the chlorine into soluble alkali chlorides. By decreasing the sample to 1 g (2 g if chlorine content is below 0.1 percent by mass) and increasing the temperature of the incineration to 775°C, the time of ignition can be reduced to one hour in a well ventilated muffle furnace. The ventilation of the muffle is very important in the rapid ignition method, and the correct conditions must be attained. If the material is of low ash content, the filtration of ash is not necessary. The determination of the total chloride is carried out by a modification of the Volhard's method or by the Mohr's method.

The use of small capsules allows several samples to be introduced into the muffle for incineration at the same time. Ash and chlorine determinations should not be carried out in the same muffle at the same time.

**NOTE** — Where the chlorine content is over 0.5 percent the incineration may be done at 675°C.

#### 6.1.1 Apparatus

**6.1.1.1 Capsules** — of 25 ml capacity, made of porcelain or silica. Crucibles may also be used.

**6.1.1.2 Silica plate** — 6 mm thick, to fit inside the muffle.

**6.1.1.3 Muffle furnace** — capable of holding about six capsules in a substantially uniform zone at  $775 \pm 25^\circ\text{C}$ . The ventilation should be such as to give about five air changes per minute.

NOTE — The necessary rate of air change can be obtained by fitting a chimney about 20 cm high to the back of the muffle, and by leaving the front door of the muffle open by 1.25 cm. If the chimney cannot be fitted to the back of the muffle, the required ventilation can be obtained by fitting an insulating brick as a door, leaving a clearance of 12.5 sq cm as air inlet, and by carrying a silica tube passing to the back of the muffle to withdraw air, which is vented through a vertical light alloy tube 2.5 cm in diameter and 40 cm in length also fitted into the insulating brick. The ventilation rate may be checked by using a Pilot tube or by so providing that six 2 g-samples of coal can be ashed completely in an hour.

**6.1.1.4 Calibrated thermocouple**

**6.1.2 Reagents**

**6.1.2.1 Eschka mixture** — Mix two parts by mass of light, calcined, magnesium oxide with one part of anhydrous sodium or potassium carbonate. The mixture should entirely pass 212-micron IS Sieve and its bulk density should not be greater than 0.50 g per ml. To determine the bulk density, place 50 g of the mixture in a 250-ml graduated cylinder; hold the cylinder in a vertical position and tap it gently 100 times on a bench or table top. Measure the volume occupied by the mixture.

**6.1.2.2 Concentrated nitric acid** — relative density 1.42 (see IS: 264-1976\*), stored in a dark bottle.

**6.1.2.3 Standard silver nitrate solutions** — 0.025 N and 0.05 N. Crush and dry silver nitrate crystals at  $125^\circ\text{C}$  for 2 to 3 hours, dissolve exactly 4.247 2 g and 8.494 4 g in small quantities of water and make each up to 1 000 ml.

**6.1.2.4 Nitrobenzene** — light in colour.

**6.1.2.5 Ferric alum indicator** — saturated solution in water, sufficient nitric acid being added to remove the brown colour, if any.

**6.1.2.6 Standard potassium thiocyanate solution** — approximately 0.02 N. Dissolve about 3.5 g of potassium thiocyanate in water, make up to 1 000 ml, standardize by titration against standard silver nitrate solution and adjust the strength to approximately 0.02 N.

**6.1.2.7 Potassium chromate indicator** — Dissolve one gram of potassium chromate in 20 ml of water.

**6.1.3 Procedure**

**6.1.3.1** Conduct a blank determination on 5 g of Eschka mixture incinerated in the muffle furnace at the same time as the samples, the

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\*Specification for nitric acid (second revision).

blank being subsequently treated in the same manner as an actual sample. The purpose of the blank is not only to test the reagents but also the chlorine content of the laboratory atmosphere; blanks should therefore be made every time when chlorine is determined.

**6.1.3.2** Weigh accurately about one gram of the air-dried coal, or two grams of air-dried coal, or two grams of coke, ground to pass 212-micron IS Sieve in a scoop and transfer it to a capsule containing three grams of Eschka mixture. Mix intimately, using a small metal spatula, and cover with two grams of Eschka mixture. Place the capsule on the silica plate and introduce the whole into the muffle furnace previously raised to about 800°C.

- a) When the chlorine content of coal is under 0.1 percent, the mass of coal should be increased to two grams; removal of the ash by filtration will then be necessary if the ash content is high.
- b) When multiple tests are carried out and several capsules are being introduced at a time, the initial temperature of the muffle furnace should be higher, say 850°C, as the large thermal capacity of the silica plate and capsules causes considerable drop in the temperature of the muffle furnace. The temperature of the muffle furnace during the incineration of samples should be  $775 \pm 25^{\circ}\text{C}$  and should be checked with a calibrated thermocouple to avoid over-heating.

**6.1.3.3 Volhard's method** — Transfer the incinerated mixture to a beaker, and add carefully a small quantity of hot water and 20 ml of concentrated nitric acid. Cover the beaker with a large watch-glass. To help dissolution, shake or stir if there are some undissolved particles. Filter the solution into a conical flask through a rapid filtering, hardened, double acid-washed filter paper of negligible ash content. This is unnecessary when one gram samples of low-ash coal are used. Wash the paper with a small quantity of hot water ( say four lots of 5 to 10 ml each ) and then add 20 ml of silver nitrate solution ( 0.025 N ), from a pipette to the beaker. Protect from light and allow the conical beaker and its contents to stand for 15 minutes. Cool, if necessary, and add 5 to 10 ml of nitrobenzene. Shake the solution for one minute, add about 8 to 10 drops of ferric alum indicator and titrate with standard potassium thiocyanate solutions; the end-point of the titration being taken as reached when the solution becomes faintly orange-pink in colour.

**6.1.3.4 Mohr's method** — Alternatively to the method described above, transfer the incinerated residue to a beaker using 20 ml of hot-water to rinse the capsule. Crush the residue in the beaker with a flat-end glass rod, heat to boiling and filter into a conical flask using a filter paper pad or a fast filter paper. Wash the residue with five 5-ml portions of hot water, collecting the washings in the conical flask. Neutralize the solution with nitric acid, add 10 drops of potassium chromate solution and titrate

with silver nitrate solution ( 0.05 N). The end-point is a change from yellow to red-brown.

NOTE — A drop of methyl red or a piece of litmus paper may be used to indicate neutralization of the solution.

#### 6.1.4 Calculation and Reporting of Results

##### a) Volhard's method

$$\text{Chlorine, percent by mass} = \frac{(b - a) 3.546 F}{M}$$

where

$b$  = the volume in ml of standard potassium thiocyanate solution used in the blank;

$a$  = volume in ml of standard potassium thiocyanate solution used in the determination;

$F$  = normality of the standard potassium thiocyanate solution; and

$M$  = mass in g of the material taken for the test.

##### b) Mohr's method

$$\text{Chlorine, percent by mass} = \frac{(X - Y) \times 0.1775}{M}$$

where

$X$  = volume in ml of standard silver nitrate solution used in the experiment;

$Y$  = volume in ml of standard silver nitrate solution used in the blank; and

$M$  = mass in g of the material taken for the test.

## 7. ARSENIC IN COAL

**7.0 General** — The coal sample is incinerated with a mixture of magnesium oxide, sodium carbonate and potassium nitrate. After the incineration the arsenates are reduced to arsine which is absorbed in silver diethyl dithiocarbamate solution and its absorbance measured at the wave length of 540 nm using water as a reference liquid.

### 7.1 Apparatus

**7.1.1 Muffle Furnace** — well ventilated, capable of maintaining a temperature of  $675 \pm 25^\circ\text{C}$ .

**7.1.2 Crucible** — made of silica.

**7.1.3 Strips** — Cut paper strips 11.5 cm long from Whatman No. 21 or No. 42 filter paper. For arsenic values up to 20 parts of arsenious oxide per million of coal, make the strips exactly 0.25 cm wide, and for higher values 0.50 cm wide. It is important that these widths should be adhered to as accurately as possible.

**7.1.4 Evolution and Absorption Apparatus** — It consists of a conical flask *A* of 100 ml capacity for evolution of arsine, a connecting tube *B* to trap hydrogen sulphide, and absorption tube *C* with a spherical or conical ground glass joint. A spring clip may be used to ensure firm joint between the connecting tube *B* and absorption tube *C* when a spherical joint is used. Suitable assembly of apparatus is shown in Fig. 3.

## 7.2 Reagents

**7.2.1 Fusion Mixture** — containing 10 parts of magnesium oxide, 5 parts of sodium carbonate (anhydrous) and 3 parts of potassium nitrate.

**7.2.2 Concentrated Sulphuric Acid** — see IS: 266-1977\*.

**7.2.3 Methyl Red Indicator** — Dissolve 0.1 g of methyl red in 60 ml of rectified spirit and dilute with water to 100 ml.

**7.2.4 Ammonium Hydroxide** — relative density about 0.90.

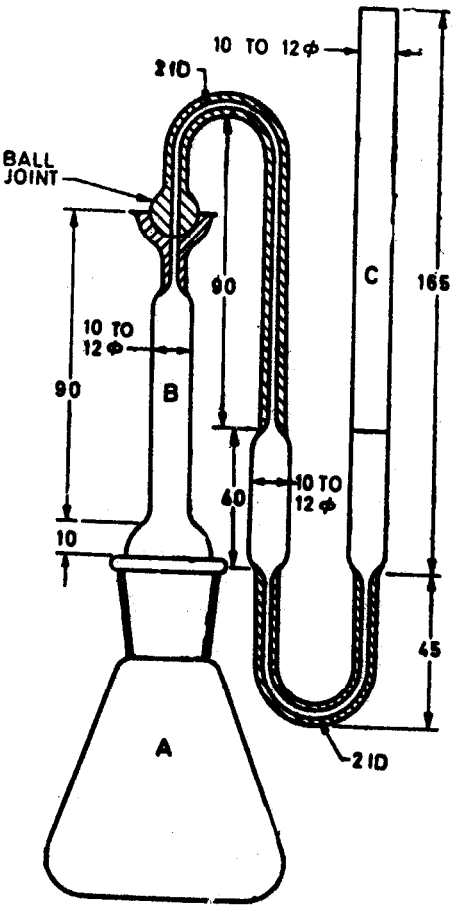
## 7.3 Procedure

**7.3.1** Take an accurately weighed amount of about one gram of the material ground to pass 212-micron IS Sieve and mix thoroughly in a silica crucible with two grams of the fusion mixture. Place the crucible in a cold muffle furnace, raise the temperature to  $675 \pm 25^\circ\text{C}$  during 70 to 90 minutes, continue heating at this temperature for a further 90 minutes period, and then examine the contents of the crucible for unburnt matter. Continue the ignition, if necessary, until the combustion is complete. Several ignitions may be carried out simultaneously.

**7.3.2 Extraction and Reduction of Arsenates** — Transfer the residue with the help of a glass rod in small portions to a hot solution of 3 ml of concentrated sulphuric acid in 10 ml of water contained in a 100-ml conical flask, finally rinsing the crucible with about 10 ml of water from a fine jet and adding the rinsing to the flask. Boil the liquid gently and assist the solution of the solid by crushing it with a flat-end glass rod. When the solvent action has been completed leaving only a very small quantity of insoluble matter, dilute to approximately 30 ml and cool to room temperature. Add a drop of methyl red indicator solution, followed by ammonium hydroxide solution drop by drop until there is one drop in excess. Proceed further as prescribed in 5.2 of IS: 2088-1971† and determine the arsenic content of the material.

\*Specification for sulphuric acid (second revision).

†Methods for determination of arsenic (first revision).



All dimensions in millimetres.

FIG. 3A ASSEMBLY OF APPARATUS FOR DETERMINATION OF ARSENIC



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